

PATENT SPECIFICATION

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(54) ETCHANTS

(71) We, SHIPLEY COMPANY INC., a Corporation organised and existing under the Laws of the State of Massachusetts, United States of America, of 2300 Washington Street, Newton, Massachusetts, U.S.A., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to acidified peroxide etchants containing a molybdenum compound to increase the rate of etching.

Peroxide etchants are known in the art and described in Plating, "Surface Treatment of Metals with Peroxygen Compounds", Vol. 42, pg. 561, (1955). Such etchants use dilute acids such as sulfuric, nitric, phosphoric or acetic and are activated to enhance etching by addition of oxygen release compounds such as hydrogen peroxide or other peroxy, persulfate or perborate compounds. Such etchants display good stability and are effective in acid and alkaline solution.

Activation of dilute acid etchants with hydrogen peroxide is most attractive due to low cost and, when used for etching copper, the ease of electrolytic copper recovery from the spent etchant prior to disposal. However, the utility of such hydrogen peroxide etching solutions is minimized due to catalyzed decomposition of hydrogen peroxide caused by etched metal ions or other transitional metal ions in solution and a slow etch rate, typically 1 mil of copper from 1 ounce copper clad laminate in 20 to 25 minutes at 120°F.

To limit the metal ion catalyzed decomposition disadvantage, a number of stabilizers are used in the prior art. These include phenacetin; sulfathiazole; saturated dibasic acids of four to twelve carbon atoms such as adipic, succinic, glutamic and malic acids; phenylurea; benzoic acid and hydroxy benzoic acids; thiourea and derivatives thereof; and substituted aromatic sulfonic acids, sulfamic acids, sulfolenes, sulfonanes, sulfoxides, and sulfones.

We have discovered that by addition of a molybdenum compound to an acidified peroxide etchant, particularly a hydrogen peroxide etchant, there results a substantially improved metal etch rate. According to the present invention, therefore, we provide a stabilised etch solution for etching metals comprising an acid solution of an oxidant combination of a peroxide and molybdenum, the molybdenum being present in an amount sufficient to increase the etch rate above that of a corresponding etch solution containing no molybdenum.

Moreover, in accordance with a preferred embodiment of this invention using an arylsulfonic acid stabilizer, there is provided an etchant having the aforesaid advantages and also possessing enhanced bath stability due to a decreased rate of peroxide decomposition without substantial decrease in the etch rate, regardless of the concentration of etched copper. Moreover, when sulfuric acid is used as the acid too etch copper, etched copper crystallizes as substantially pure cupric sulfate-pentahydrate at room temperature. This permits regenerative replenishment of the etch solution by cooling to room temperature with addition of more peroxide and stabiliser.

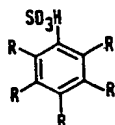
Though a molybdenum compound added to the etchant primarily exalts etch rate, it has also been found that in high concentrations, it reduces attack on tin electroplate. The particular molybdenum compound used does not appear to be critical provided it is sufficiently soluble in solution, typical molybdenum compounds including, by way of example, molybdenum tetrabromide, molybdenum trichloride, molybdenum oxytetrachloride, molybdenum oxydichloride, molybdenum oxypentachloride, molybdenum oxytetrafluoride, molybdenum trisulfide and molybdic acid, and its salts such as sodium molybdate, and ammonium molybdate. It should be recognized that those

compounds having limited solubility in the etchant are less preferred as they must be used in lesser quantities.

The concentration of the molybdenum compound is not critical, it having been found that rate increases rapidly with small additions of molybdenum and then levels off as the concentration increases. Thus, exaltation of the etch rate occurs when the molybdenum concentration is as low as 0.1 grams per liter (as molybdenum metal) and increases as the concentration increases up to about 6 grams per liter. Thereafter, the etch rate holds about level with increasing concentrations of molybdenum e.g. up to 8 grams per litre. However, as the concentration increases—e.g. above 10 grams per liter—there is a marked decrease in attack on tin electroplate. However, the advantage of this reduced attack is at the expense of stability as it has been found that the higher concentration of molybdenum tends to cause accelerated catalytic decomposition of the peroxide in etchants containing substantial quantities of dissolved copper even in the presence of stabilizers. In view of the above, the preferred concentration of the molybdenum compound is that amount that increases the etch rate without significantly increasing the rate of catalytic decomposition of peroxide. This concentration preferably varies between about 0.1 and 10 grams per liter as molybdenum metal and more preferably varies between 1 and 8 grams per liter. As should be apparent to those skilled in the art, the exact amount is dependent upon the specific etch solution to which the molybdenum is added and its concentration of dissolved copper.

In accordance with the invention, the etchant is stabilized to prevent catalytic decomposition caused by addition of the molybdenum compound. Though most stabilizers such as those disclosed above provide some benefit, in the most preferred embodiment of the invention, the stabilizer is an aryl sulfonic acid.

The aryl sulfonic acids contemplated conform to the following general formula:



where any two adjacent R's may form a second aryl nucleus and where said R's, not part of an aryl nucleus, are individually selected from hydrogen, polar groups such as hydroxyl, sulfonyl, carboxyl, halo, nitro, diazo and amino radicals, aliphatic groups having up to six carbon atoms including cycloaliphatic and alkyl, alkenyl and alkynyl groups, and the aforesaid aliphatic groups substituted with the aforesaid polar groups. Preferably, at least one of said R's is a polar group so that the arylsulfonic acid has enhanced solubility in the etching solution and can be dissolved in the solution in the amounts set forth above in the preferred concentration ranges.

Specific examples of arylsulfonic acids include, by way of illustration, sulfosalicylic acid, *p*-phenolsulfonic acid, *p*-toluenesulfonic acid, 1,4 - benzene disulfonic acid, 4 - hydroxy naphthalene sulfonic acid, 1 - ethyl - 4 - sulphobenzene, 1 - propyl - 3-chloro - 6 - sulphonaphthalene, 4 - nitro - benzenesulphonic acid, 2,6 - naphthalene disulfonic acid, 1 - amino - 2 - naphthalene sulfonic acid, 4 - cyclohexyl benzene sulfonic acid, 1 - diazo - 2 - naphthol - 4 - sulfonic acid and mixtures thereof.

From the aforesaid, it can be seen that in accordance with the invention, the etchant comprises the acid; a peroxide, especially hydrogen peroxide; a stabilizer; and a molybdenum compound. The concentration of each is not critical. For each of the peroxide and the acid, the concentration can vary from about 1 to 40% by weight but preferably varies from 2 to 30% by weight and most preferably, varies from 5 to 15% by weight. With respect to the stabilizer, particularly the aryl sulfonic acid stabilizer, its concentration is related to the impurity concentration (the dissolved transition metal and molybdenum compound). Since the concentration is difficult to predict, it is difficult to define precisely the required concentration of stabilizer. For purposes of setting forth guidelines only, the concentration of stabilizer may vary from as low as 1 gram per liter of solution to the solubility limit of the stabilizer. Preferably, the concentration varies between 1 and 50 grams per liter and more preferably, from 3 to 25 grams per liter. Finally, the concentration of the molybdenum compound has been discussed above.

Using the etchant of the invention to etch copper, as etching begins, at the normal operating temperature of 70°—120°F, the bath changes in color from clear to brown to blue-green. At 120°F, the bath will dissolve about 78 g of copper per litre. Maintaining the hydrogen peroxide concentration within 60—100% of its initial bath

make-up permits continued operation until saturation with dissolved copper. Allowing the bath to cool to room temperature induces crystallisation of copper as substantially pure cupric sulfate pentahydrate crystals using sulfuric acid in the acid, which may be recovered by filtration. Readjustment of the peroxide content by addition of both

peroxide and stabiliser acid solution makes the bath suitable for reuse.
This invention will be better understood by reference to the following examples:
The base etchant formulation for examples was as follows until indicated otherwise:

Hydrogen peroxide (35% wt.)	100 ml
Phenol sulfuric acid (65% wt.)	20 gm
Sulfuric acid (50% wt.)	96 ml
Distilled water	to 1 litre

Examples 1—8

The above etchant was used with ammonium molybdate added in varying concentration. One ounce copper clad phenolic resin was etched at 120°F. The table below sets forth the concentration of the ammonium molybdate in the etchant and the time required to completely strip the copper from the phenolic substrate.

Example No.	Molybdate concentration (gm/litre)	Molybdenum concentration (gm/litre)	Time (min)	H ₂ O ₂ /M _o
1	0	0	20 +	
2	4	1.96	4	17.85
3	8	3.72	3½	8.93
4	12	5.88	2½	5.95
5	16	7.84	2½	4.46
6	20	9.8	2½	3.57
7	24	11.75	2½	2.98
8	26 ⁽¹⁾	12.73	—	

⁽¹⁾exceeded solubility limit.

The above composition attacks tin electroplate at the lower concentration of ammonium molybdate but as the concentration increases, the attack on tin electroplate is reduced such that with Examples 6 and 7, there is negligible attack. However, the rate of peroxide decomposition in Examples 6 and 7 is much greater than, for instance, Examples 1 to 3, particularly when the etchant has been used to dissolve significant amounts of copper. In the absence of phenolsulfonic acid in the examples, the peroxide loss would have been significant. As an additional and preferred alternative, sodium molybdate can be substituted for ammonium molybdate.

The above procedure was repeated fixing the concentration of the ammonium molybdate at 15 gm/liter, but varying the concentration of hydrogen peroxide with results as follows:

Example No.	Peroxide Concentration (ml)	Time (min.)	H ₂ O ₂ /M _o
9	100=35 g/l	3½	4.76
10	200=70 g/l	2½	9.52
11	300=105 g/l	1½	14.29

Examples 12—16

The above procedure was repeated again fixing the ammonium molybdate concentration at 15 gm/liter but varying the sulfuric acid concentration with results as follows:

Example No.	Sulfuric Concentration (ml.)	Time (min.)
12	10	2½
13	25	2½
14	50	2½
15	200	3

The following stabilizers can be substituted for phenol sulfonic acid though phenol sulfonic acid is preferred and the arylsulfonic acids are preferred to other stabilizers. The stabilizers were all added in amounts of 6 grams per liter.

	Example No.	Stabilizer	
	16	sulfo salicyclic acid	
	17	phenol sulfonic acid	
	18	1,3 - benzene disulfonic acid	
5	19	1 - diazo - 2 - naphthol - 4 - sulfonic acid	5
	20	2,6 - naphthalene disulfonic acid	
	21	1 - amino - 2 - naphthalene sulfonic acid	
	22	phenacetin	
	23	phenylurea	
10	24	benzoic acid	10
	25	adipic acid	

Examples 26—28

The following formulation was made:

	Hydrogen peroxide(35%)	100 ml	
15	Hydrochloric acid (conc.)	variable	15
	Molybdic acid	10 gm	
	Phenol sulfonic acid	20 gm	
	Water	to 1 liter	

Each rate was determined following the procedures above.

20	Example No	Hydrochloric acid (ml/l)	Time (min.)	20
	26	100	25	
	27	200	8	
	28	300	9	

25 The following examples illustrate etchants prepared with compounds which release hydrogen peroxide. The formulation of each etchant was as follows: 25

Example 29

	Sodium peroxide	20 gm	
	Sulfuric acid (13.8N)	250 ml	
30	Molybdic acid	20 gm	30
	Phenolsulfonic acid	20 gm	
	Water	to 1 liter	

Example 30

	Sodium perborate	20 gm	
	Sulfuric acid (13.8N)	250 ml	
35	Molybdic acid	20 gm	35
	Phenolsulfonic acid	20 gm	
	Water	to 1 liter	

40 The above two formulations could be used as etch solutions but were not sufficiently stable for use as a commercial formulation. 40

WHAT WE CLAIM IS:—

1. A stabilised etch solution for etching metals comprising an acid solution of an oxidant combination of a peroxide and molybdenum, the molybdenum being present in an amount sufficient to increase the etch rate above that of a corresponding etch solution containing no molybdenum. 45
2. A solution according to Claim 1 wherein the acid is sulfuric acid, hydrochloric acid, acetic acid or phosphoric acid.
3. A solution according to Claim 2 wherein the acid is sulfuric acid.
4. A solution according to any of Claims 1 to 3, wherein the peroxide is hydrogen peroxide. 50
5. A solution according to any of Claims 1 to 4 wherein the stabilizer for the etch is an aryl sulfonic acid.
6. A solution according to Claim 5, wherein the sulphonic acid is phenol sulphonic acid.
7. A solution according to any of Claims 1 to 6, wherein the molybdenum com- 55

5 pound is present in an amount of from 0.1 grams molybdenum per liter to the solubility limit of the compound.

8. A solution according to Claim 7 where the concentration of the molybdenum compound is from 1 to 8 grams molybdenum per litre of solution.

5 9. A solution according to any of Claims 1 to 8 where the molybdenum compound is molybdic acid or a salt thereof.

10. A solution according to Claim 7 in which the ratio by weight of peroxide to molybdenum is at least 3:1.

10 11. A solution according to Claim 1 substantially as herein described.

12. A stabilised acid peroxide etch solution containing a molybdenum compound substantially as described in any of Examples 2 to 30. 10

13. A method of etching comprising contacting a metallic surface with an etch solution according to any of Claims 1 to 12.

15 14. A method according to Claim 13, as a continuous process including the steps of etching copper cooling to precipitate dissolved copper values, separating the precipitate from the etchant, replenishing the etchant and repeating the process. 15

MARKS & CLERK.

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